



PHYS393 – Statistical Physics

Part 1: Principles of Statistical Mechanics and the Boltzmann Distribution

Introduction

The course is comprised of six parts:

1. Principles of statistical mechanics, and the Boltzmann distribution.
2. Two examples of the Boltzmann distribution.
3. The Maxwell-Boltzmann gas.
4. Identical fermions: the Fermi-Dirac distribution.
5. Identical bosons: the Bose-Einstein distribution.
6. Low temperature physics.

The goal of statistical mechanics is to understand how the macroscopic properties of materials arise from the microscopic behaviour of their constituent particles.

Examples include:

- specific heat capacity and its variation with temperature;
- the entropy of a sample of material, and its relationship with temperature and internal energy;
- the magnetic properties of materials.

Part 1: the Boltzmann distribution

In the first part of this course, we will introduce the fundamental principles of statistical mechanics. We will use these principles to derive the Boltzmann distribution, which tells us how particles in a system in thermal equilibrium are distributed between the energy levels in the system:

$$P(\varepsilon) = \frac{1}{Z} g(\varepsilon) e^{-\frac{\varepsilon}{kT}} \quad (1)$$

In this equation, $P(\varepsilon)d\varepsilon$ is the probability that a constituent particle has energy in the (small) range ε to $\varepsilon + d\varepsilon$; $g(\varepsilon) d\varepsilon$ is the number of energy states between ε and $\varepsilon + d\varepsilon$; k is a fundamental physical constant (the Boltzmann constant); T is the thermodynamic temperature; and $Z = Z(T)$ is a function of temperature, known as the “partition function” that normalises the probability:

$$\int_0^\infty P(\varepsilon)d\varepsilon = 1. \quad (2)$$

The Boltzmann distribution turns out to be the basis of many important properties of materials. It also helps us to understand the physical significance of concepts arising in thermodynamics, including temperature and entropy.

The Boltzmann distribution relies on a number of assumptions and approximations. We shall consider these in some detail.

In the later parts of this course, we shall consider what happens if we change some of the assumptions. This will lead to variations on the Boltzmann distribution: of particular significance are the Fermi-Dirac distribution and the Bose-Einstein distribution.

Macrostates and microstates

A *macrostate* specifies a system in terms of quantities that “average” over the microscopic constituents of the system. Examples of such quantities include the pressure, volume and temperature of a gas. Such quantities only make sense when considered in a system composed of very large numbers of particles: it makes no sense to talk of the pressure or temperature of a single molecule.

A *microstate* specifies a system in terms of the properties of each of the constituent particles; for example, the position and momentum of each of the molecules in a sample of gas.

A key concept of statistical mechanics is that many different microstates can correspond to a single macrostate. However, specifying the macrostate imposes constraints on the possible microstates. Statistical mechanics explores the relationship between microstates and macrostates.

The Boltzmann distribution tells us the distribution of particles between energies in a system. In a classical system, there is a continuous range of energies available to the particles; but in a quantum system, the available energies take discrete values.

In this course, we shall generally consider quantum systems. This is more realistic - but it also turns out to be somewhat easier to consider systems with discrete energy levels, than systems with continuous ranges of energy.

Let us first introduce the energy levels in two example cases:

- a collection of harmonic oscillators;
- a collection of magnetic dipoles in an external magnetic field.

Energy levels in an harmonic oscillator

To find the allowed energies for a quantum system, we have to solve Schrödinger's equation:

$$\hat{H}\psi = \varepsilon\psi \quad (3)$$

where ψ is the wave function of the system, ε is an allowed energy, and \hat{H} is the Hamiltonian operator. In one dimension,

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx^2} + V(x). \quad (4)$$

For an harmonic oscillator, the potential $V(x)$ is given by:

$$V(x) = \frac{1}{2}kx^2 \quad (5)$$

where k is a constant. Schrödinger's equation is then:

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \left(\varepsilon - \frac{1}{2}kx^2 \right) \psi = 0. \quad (6)$$

The energy levels in an harmonic oscillator are found by solving Schrödinger's equation (6):

$$\frac{\hbar^2}{2m} \frac{d^2\psi}{dx^2} + \left(\varepsilon - \frac{1}{2} kx^2 \right) \psi = 0.$$

Fortunately, in statistical mechanics, we do not need a full solution; in this course, we don't need to know the wave function. We do, however, need to know the allowed energy levels. This is a standard problem in quantum mechanics text books. The allowed energy levels are given by:

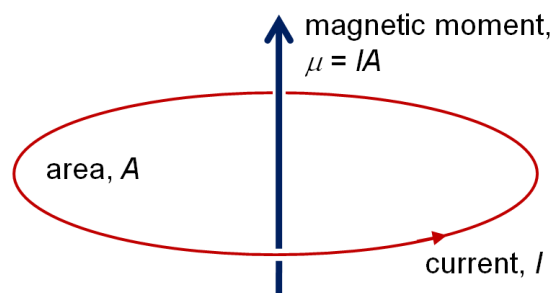
$$\epsilon_j = \left(j + \frac{1}{2} \right) \hbar\omega, \quad (7)$$

where j is zero or a positive integer, $j = 0, 1, 2, 3, \dots$, and:

$$\omega = \sqrt{\frac{k}{m}}. \quad (8)$$

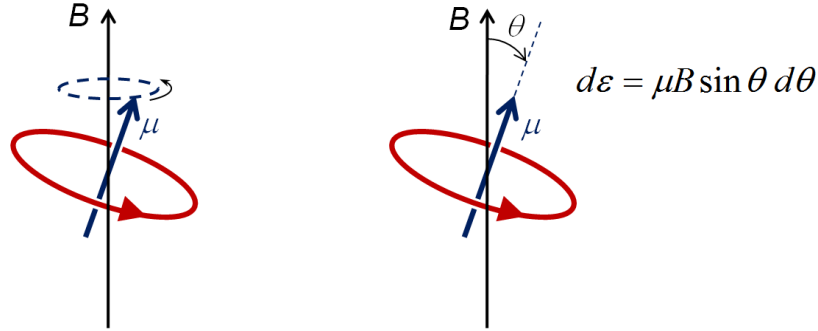
Energy levels: magnetic dipole in a magnetic field

As a second example, we consider a magnetic dipole in an external magnetic field. Classically, a magnetic dipole is generated by a loop of wire carrying an electric current:



The magnetic moment of the dipole is equal to the area of the loop multiplied by the current.

Consider a magnetic dipole in an external magnetic field. The external field exerts a force on the current in the dipole, leading to a precession of the dipole around the external field, in which the angle between the dipole and the field remains constant. Changing the angle between the dipole and the field requires energy.



The energy ε of a classical magnetic dipole μ at angle θ to an external magnetic field B is:

$$\varepsilon = \int_0^\theta \mu B \sin \theta d\theta = \mu B (1 - \cos \theta). \quad (9)$$

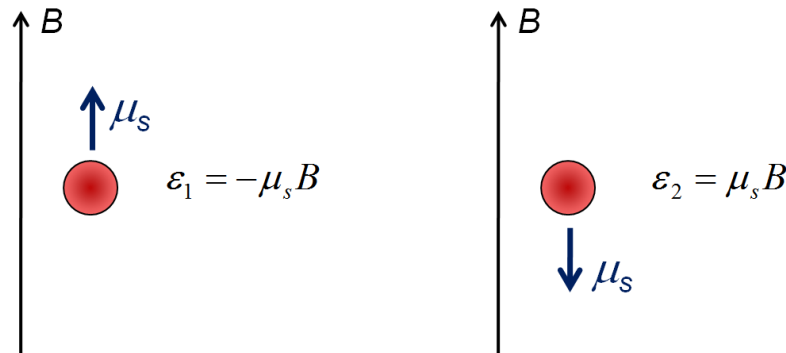
Individual particles (electrons, atoms etc.) can also have a magnetic moment, which is related to the intrinsic angular momentum, or spin, of the particle. Since the spin of a quantum system can take only discrete values, the magnetic moment of such a particle can also take only discrete values:

$$\mu = \frac{e\hbar}{2m} g_s s, \quad (10)$$

where e is the charge and m the mass of the particle, s is the spin number, and g_s a constant (the Landé g -factor, ≈ 2 for an electron). For a spin- $\frac{1}{2}$ particle, there are only two values for s , $s = \pm \frac{1}{2}$.

For a spin- $\frac{1}{2}$ charged particle in an external magnetic field, there are just two possible energy states, corresponding to having the magnetic moment parallel or anti-parallel to the magnetic field. The difference in energy between the energy states is:

$$\Delta\varepsilon = 2\mu_s B. \quad (11)$$



Energy levels: interactions between particles

So far, we have considered the energy levels of individual particles. But in statistical mechanics, we are concerned with systems consisting of very large numbers of particles. If the particles do not interact, they cannot exchange energy, and nothing interesting happens: a system in a particular microstate, specified by the energy of each particle, will remain in that microstate.

A system in which the particles interact is much more interesting: if the particles can exchange energy, then the system can achieve an equilibrium in which the microstate is essentially independent of the initial microstate. It is such an equilibrium that is described by the Boltzmann distribution.

However, if the interactions between particles are very strong, then the forces on the particles are significantly different from those on the isolated particles we have so far considered. We cannot assume that the energy levels are the same, and it becomes very difficult, or impossible, to analyse the system.

How do we describe interactions between particles in a quantum system? Let us consider two particles in an external field, described by a potential $V(x)$.

Let x_1 be the coordinate of the first particle, and x_2 be the coordinate of the second particle. The Hamiltonian for the system is:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m} \frac{d^2}{dx_2^2} + V(x_1) + V(x_2). \quad (12)$$

The solution to Schrödinger's equation in this case is:

$$\psi(x_1, x_2) = \psi_1(x_1)\psi_2(x_2), \quad (13)$$

where $\psi_1(x_1)$ and $\psi_2(x_2)$ are solutions to the single-particle Schrödinger equation (6).

If the particles interact, then we need to include a potential $\epsilon V_{int}(x_1, x_2)$ that describes this interaction. ϵ is a small number that characterises the strength of the interaction.

The Hamiltonian is now:

$$\hat{H} = -\frac{\hbar^2}{2m} \frac{d^2}{dx_1^2} - \frac{\hbar^2}{2m} \frac{d^2}{dx_2^2} + V(x_1) + V(x_2) + \epsilon V_{int}(x_1, x_2). \quad (14)$$

Solution of this equation is much more complicated than before. However, if ϵ is small enough, then we can assume that the solution can be written:

$$\psi(x_1, x_2) = \psi_1(x_1)\psi_2(x_2) + \epsilon \psi_{12}(x_1, x_2) + O(\epsilon^2). \quad (15)$$

That is, we can express the total wave function as a Taylor series in ϵ .

Strictly speaking, we should now calculate the energy spectrum for the system consisting of both particles. However, if ϵ is small, we can assume that the energies of the system are given by:

$$\varepsilon_k = \varepsilon_{j1} + \varepsilon_{j2} + \epsilon \varepsilon_{j1,j2} + O(\epsilon^2). \quad (16)$$

In the limit of weak interaction (small ϵ), the energy levels of the two-particle system are simply found from sums of the energy levels of the single-particle system.

This is very helpful, since it allows us to analyse a system of many particles using the energy levels corresponding to a single-particle system. However, we must assume that the interactions between the particles are very weak.

Basic assumptions of statistical mechanics

As we develop the principles of statistical mechanics, we shall consider systems composed of a number of constituent particles. To allow us to proceed, we shall make the following assumptions:

- The number of particles in the system is very large (typically of order 10^{23}).
- The number of particles in the system is fixed.
- The volume of the system is fixed (i.e. no *work* is done on or done by the system).
- Particles can exchange energy, but interactions between particles are very weak.

Recall that the last assumption allows us to treat the energy levels of the system as the sum of the energy levels of a corresponding single-particle system, while allowing the system to move between different microstates.

A further key assumption is the principle of *equal a priori probabilities*. This states that:

A system in thermal equilibrium in a given macrostate may be found with equal likelihood in any of the microstates allowed by that macrostate.

Applying “equal a priori probabilities”: energy level populations

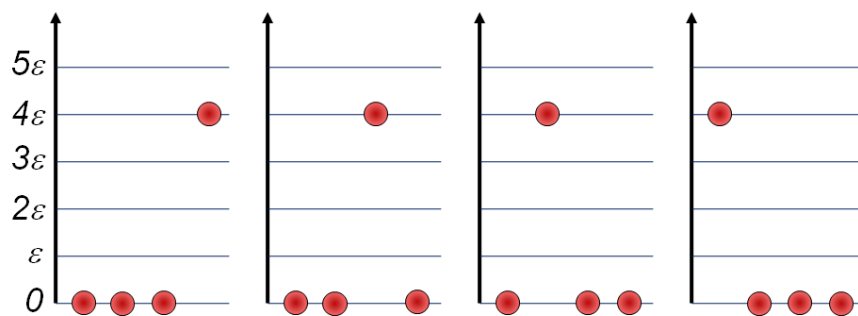
The principle of equal a priori probabilities can be used on its own to derive some interesting results in specific cases. For example, consider a system consisting of just four particles, each of which can have an energy which is an integer multiple of ϵ , i.e. $0, \epsilon, 2\epsilon, 3\epsilon, 4\epsilon \dots$

We can use equal a priori probabilities to find the average number of particles with each of the allowed energies (“average population”), for a given total energy.

In this case, the macrostate is defined by the total number of particles, and the total energy. Let us specify a macrostate with total energy 4ϵ . First, we find the microstates...

A microstate is specified by the energy of each of the particles in the system. It is convenient to group the microstates into *distributions*: microstates within the same distribution have the same number of particles in each of the allowed energy levels.

For example, one distribution in the present case has three particles with zero energy, and a single particle with energy 4ε . There are four microstates with this distribution:



Each microstate is specified by the energy of each of the four particles. Given that the total energy of the system is 4ε , we can draw a table listing the allowed distributions, and the number of microstates t within each distribution:

Distribution	n_0	n_1	n_2	n_3	n_4	No. microstates
1	3	0	0	0	1	$t_1 = 4$
2	2	1	0	1	0	$t_2 = 12$
3	2	0	2	0	0	$t_3 = 6$
4	1	2	1	0	0	$t_4 = 12$
5	0	4	0	0	0	$t_5 = 1$

The value of n_j gives the number of particles with energy ε_j ($\varepsilon_0 = 0$, $\varepsilon_1 = \varepsilon$, etc.) The value of t_n gives the number of microstates for each distinct distribution - note that we are assuming that the particles are *distinguishable*.

Applying “equal a priori probabilities”: energy level populations

Summing the values of t_j in the table on the previous slide, we find that there are 35 possible microstates allowed by the specified macrostate (four particles, total energy 4ε).

Using the principle of equal a priori probabilities, given an ensemble of systems in the specified macrostate, the average number of particles with zero energy will be:

$$\bar{n}_0 = \frac{4}{35} \times 3 + \frac{12}{35} \times 2 + \frac{6}{35} \times 2 + \frac{12}{35} \times 1 + \frac{1}{35} \times 0 \approx 1.71 \quad (17)$$

Similarly, we find:

$$\bar{n}_1 \approx 1.14$$

$$\bar{n}_2 \approx 0.69$$

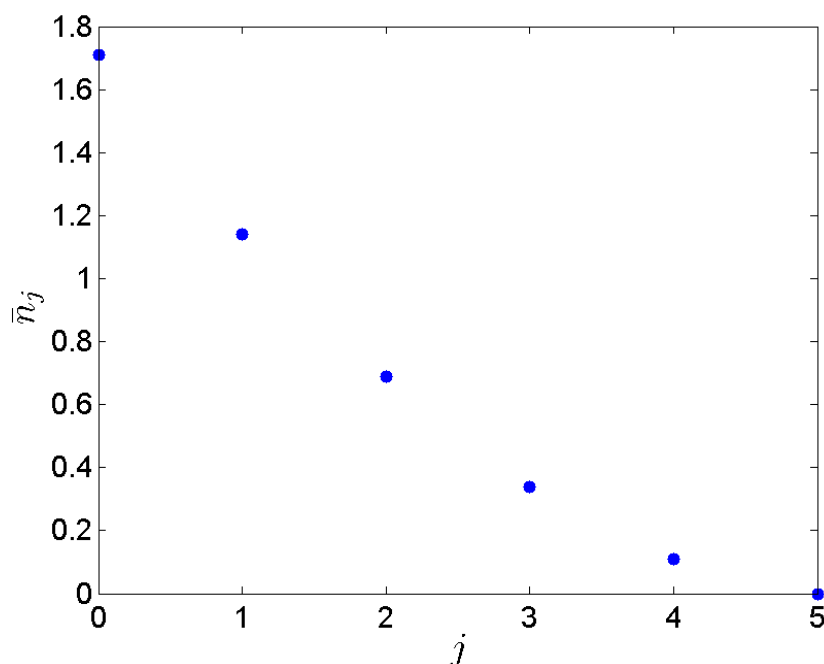
$$\bar{n}_3 \approx 0.34$$

$$\bar{n}_4 \approx 0.11$$

$$\bar{n}_5 = 0$$

Applying “equal a priori probabilities”: energy level populations

If we plot the mean population against the energy, we see an (approximately) exponential decrease... this is our first hint of the Boltzmann distribution.



In the last example, we considered a system with many energy levels, but only a small number of particles. As another example, let us consider a system with just three energy levels, but many particles. This might represent, for example, a collection of spin-1 charged particles in an external magnetic field.

Suppose that the energy levels have energy 0, ε and 2ε . The populations of each level are denoted n_0 , n_1 and n_2 , respectively. For a given macrostate, with a total of N particles, and total energy U , the populations must satisfy:

$$n_0 + n_1 + n_2 = N, \quad (18)$$

$$n_1\varepsilon + 2n_2\varepsilon = U. \quad (19)$$

Since there are two constraints, a distribution can be specified by giving the population of just one of the energy levels. For example, if we specify n_2 , then:

$$n_1 = \frac{U}{\varepsilon} - 2n_2, \quad (20)$$

$$n_0 = N - n_1 - n_2 = N - \frac{U}{\varepsilon} + n_2. \quad (21)$$

Now we need an expression for the number of microstates within each distribution...

A given distribution has N particles, with n_0 in the state with zero energy, n_1 in the state with energy ε etc.

There are $N!$ ways of arranging N particles into a set of N specified single-particle states. However, the n_0 particles with zero energy can be arranged in $n_0!$ different ways, without affecting the distribution. Similarly, for the n_1 particles with energy ε , n_2 particles with energy 2ε , etc.

Hence, the number of microstates within a given distribution is:

$$t = \frac{N!}{n_0!n_1!n_2!n_3!\dots} \quad (22)$$

Number of microstates in a three-level system

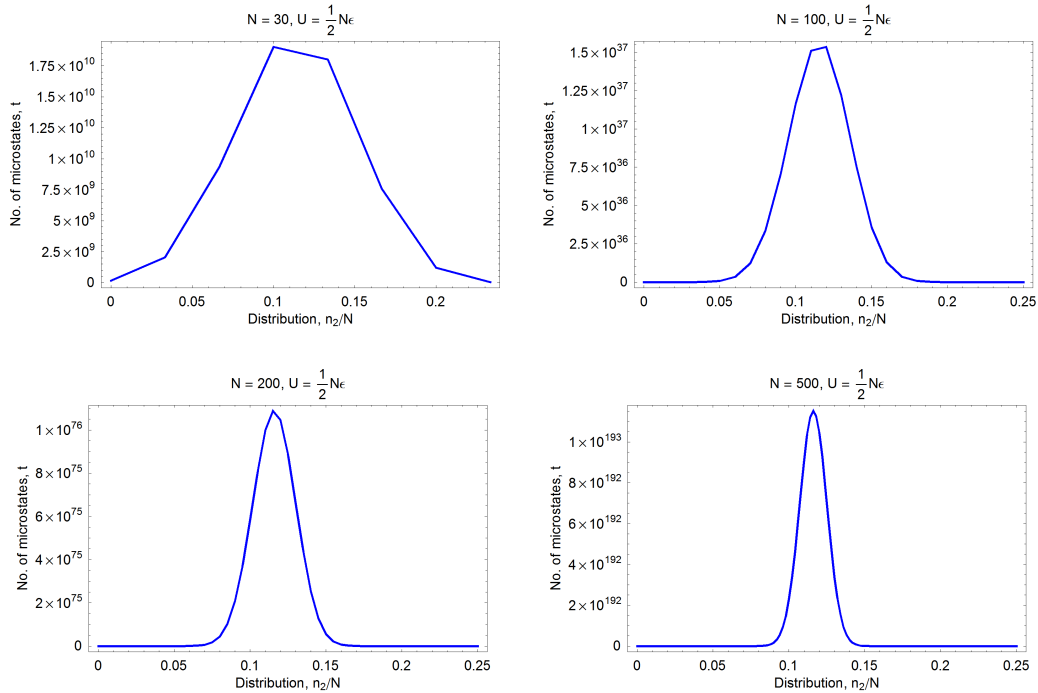
In the case of a three-level system, with N particles and total energy U , combining equations (20), (21) and (22), we find that the number of microstates in a distribution with specified n_2 is:

$$t = \frac{N!}{\left(N - \frac{U}{\varepsilon} + n_2\right)! \left(\frac{U}{\varepsilon} - 2n_2\right)! n_2!} \quad (23)$$

It is interesting to look at the number of microstates for each distribution, for a given total number of particles N , and total energy U ...

Number of microstates in a three-level system

We plot t against n_2/N , for energy $U = N\varepsilon/2$, and four cases of N , $N = 30, 100, 200$ and 500 .



Number of microstates in a three-level system

As the number of particles increases, so does the number of microstates accessible to the system. This is as we might expect. A more interesting observation is that the number of microstates per distribution becomes sharply peaked, with a small number of distributions containing many more microstates than the distributions on either side. The peak becomes sharper as the number of particles in the system increases.

We only plotted cases up to 500 particles. When the number of particles becomes truly large, of order 10^{23} or more, there is essentially a single distribution which has vastly more microstates than any other distribution.

Combined with the principle of equal a priori probabilities, we conclude that a system in thermal equilibrium is likely to be found in only one of the many distributions accessible to it. This distribution is the one with the largest number of microstates.

Before turning to the general case, let us plot the population of each level in the three-level system. Reading from the plot of the number of microstates for each distribution for $N = 500$, we see that the most probably distribution occurs for:

$$n_2 \approx 0.116N. \quad (24)$$

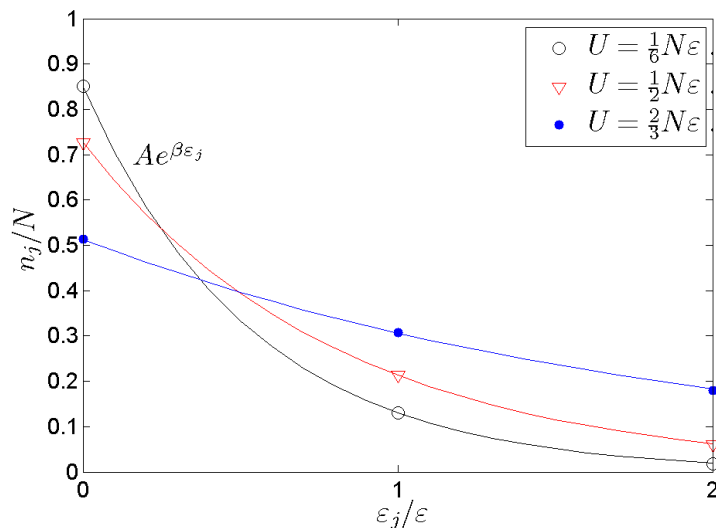
We then find from the constraints (20) and (21), that:

$$n_1 \approx 0.268N, \quad (25)$$

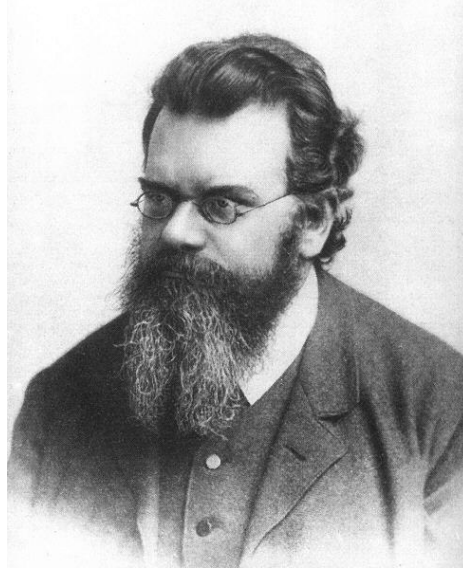
$$n_0 \approx 0.616N. \quad (26)$$

Most probable distribution

Having found the populations in the most probable distribution, we can plot them against the energy level. We calculated the populations in the case that $U = \frac{1}{2}N\varepsilon$; we can repeat the calculation for other cases, and show these on the plot as well.



In all cases, we find that the variation of population with energy fits well to an exponential curve.



Ludwig Boltzmann, 1844–1906.

Now we consider the general case, where there is an arbitrary number of energy levels, and a large number of particles. We will look for the most probable distribution, i.e. the distribution that has more microstates accessible to the system than any other. This is the distribution in which we expect to find a system in thermal equilibrium, given the basic assumptions of statistical mechanics.

Recall that a distribution is specified by a particular set of values for the populations of the energy levels, $\{n_j\}$; and that if the total number of particles in the system is N , then the number of microstates for a given distribution is:

$$t = \frac{N!}{n_1!n_2!n_3!\dots n_j!}. \quad (27)$$

To find the most probable distribution, we need to find the set of populations $\{n_j\}$ that maximises t .

Since N is very large, we can use Stirling's approximation (see Appendix B):

$$\ln N! = N \ln N - N. \quad (28)$$

Assuming that each of the values n_j is also large, we can apply Stirling's approximation further, to find:

$$\ln t = N \ln N - N - \sum_j (n_j \ln n_j - n_j). \quad (29)$$

Since N is constant, the variation of $\ln t$ with respect to variations in each of the n_j is given by:

$$d(\ln t) = - \sum_j \left(\ln n_j + \frac{n_j}{n_j} - 1 \right) dn_j = - \sum_j \ln(n_j) dn_j. \quad (30)$$

Since $\ln t$ increases monotonically with t , maximising t is the same as maximising $\ln t$. Hence, when t is a maximum (with respect to changes in the population of each of the energy levels), we have:

$$d(\ln t) = - \sum_j \ln(n_j) dn_j = 0. \quad (31)$$

However, the variations in the population levels must satisfy the constraints imposed by the macrostate. That is, the total number of particles, and the total energy must remain constant:

$$dN = \sum_j dn_j = 0, \quad (32)$$

$$dU = \sum_j \varepsilon_j dn_j = 0. \quad (33)$$

To satisfy the above equations (31), (32) and (33) simultaneously, we introduce parameters α and β (to be determined), and write:

$$-\sum_j \left(\ln(n_j) - \alpha - \beta \epsilon_j \right) dn_j = 0. \quad (34)$$

The variations in n_j are now arbitrary; and for equation (34) to be true for all dn_j , we must have:

$$\ln(n_j) - \alpha - \beta \epsilon_j = 0 \quad (35)$$

for each j . Hence, the most probable distribution (that with the largest number of microstates) is given by:

$$n_j = e^\alpha e^{\beta \epsilon_j}. \quad (36)$$

This is the Boltzmann distribution. The constants α and β are determined by the constraints:

$$\sum_j n_j = N, \quad \sum_j n_j \epsilon_j = U. \quad (37)$$

The constant α is easily eliminated. We write:

$$\sum_j n_j = \sum_j e^\alpha e^{\beta \epsilon_j} = N. \quad (38)$$

Since α is independent of j , we have:

$$e^\alpha = \frac{N}{\sum_j e^{\beta \epsilon_j}}. \quad (39)$$

This puts the Boltzmann distribution into the form:

$$n_j = \frac{N}{Z} e^{\beta \epsilon_j}, \quad (40)$$

where the *partition function* Z is given by:

$$Z = \sum_j e^{\beta \epsilon_j}. \quad (41)$$

Note that the summation extends over all energy levels.

As we expected from our analysis of the three-state system, the populations of the energy levels of a system in thermal equilibrium decrease exponentially with increasing energy:

$$n_j = \frac{N}{Z} e^{\beta \epsilon_j}.$$

The parameter β determines the rate of exponential decrease (assuming that $\beta < 0$) of the populations: the more negative the value of β the more rapid the decay. For $\beta \ll 0$, low energy states will be very highly populated compared to high energy states. For β close to zero, the distribution is more uniform.

The value of β is determined by the total energy of the system. The larger the total energy, the closer the value of β comes to zero.

Total energy and number of microstates

The parameter β that appears in the Boltzmann distribution plays another role, in relating the total energy of a system to the number of microstates accessible to the system. To derive this relationship, we begin with the number of microstates in the most probable distribution:

$$t = \frac{N!}{n_1! n_2! n_3! \dots} \quad (42)$$

Since most of the microstates accessible to a system occur in the most probable distribution, we can write for the total number of accessible microstates, Ω :

$$\Omega \approx t, \quad (43)$$

and hence, using Stirling's approximation:

$$\ln \Omega \approx N \ln N - N - \sum_j (n_j \ln n_j - n_j). \quad (44)$$

Substituting for n_j from the Boltzmann distribution (40), and using $\sum_j n_j = N$, we find:

$$\ln \Omega \approx N \ln N - \sum_j \left(\frac{N}{Z} \ln \left(\frac{N}{Z} \right) e^{\beta \varepsilon_j} + \frac{N}{Z} \beta \varepsilon_j e^{\beta \varepsilon_j} \right). \quad (45)$$

Then, using:

$$\sum_j n_j \varepsilon_j = \sum_j \frac{N}{Z} \varepsilon_j e^{\beta \varepsilon_j} = U, \quad (46)$$

we obtain:

$$\ln \Omega \approx N \ln Z - \beta U. \quad (47)$$

Since N is constant, and Z is independent of the total energy, we find:

$$\frac{\partial \ln \Omega}{\partial U} \approx -\beta. \quad (48)$$

In other words, β tells us the rate at which the number of accessible microstates increases with the energy of the system.

Statistical mechanics and thermodynamics

Equation (48):

$$\frac{\partial \ln \Omega}{\partial U} \approx -\beta$$

turns out to give an important connection between statistical mechanics and thermodynamics.

Statistical mechanics and thermodynamics approach the description of thermal systems in very different ways, one using microstates, and the other using macrostates. In thermodynamics, we have an important relationship between internal energy U , entropy S and volume V :

$$dU = T dS - p dV, \quad (49)$$

where T is the (thermodynamic) temperature and p is the pressure. We are considering systems with fixed volume, i.e. $dV = 0$, in which case:

$$dU = T dS. \quad (50)$$

Thermodynamics gives us the relationship between energy, temperature and entropy:

$$\frac{\partial S}{\partial U} = \frac{1}{T}. \quad (51)$$

Statistical mechanics gives us the relationship (48) between energy, the number of accessible microstates Ω and the distribution parameter β :

$$\frac{\partial \ln \Omega}{\partial U} = -\beta.$$

Given the above equations, it is natural to relate entropy to the number of accessible microstates:

$$S = k \ln \Omega, \quad (52)$$

and the distribution parameter β to the thermodynamic temperature:

$$\beta = -\frac{1}{kT}, \quad (53)$$

where k is a constant, with units of joules per kelvin (J/K).

Although we have not developed a formal proof, equations (52) and (53) do in fact provide an important connection between statistical mechanics and thermodynamics.



Boltzmann's grave in Vienna, engraved with the "entropy formula".

Boltzmann's constant

The equations (52) and (53) help us understand the physical significance of entropy and temperature.

The constant k , called Boltzmann's constant, essentially sets the scale of temperature. With the standard definition of the kelvin, Boltzmann's constant takes the value:

$$k \approx 1.3806 \times 10^{-23} \text{ J/K.} \quad (54)$$

Finally, we derive two useful relationships relating the energy of a system to the partition function, Z . The first involves the total internal energy, U , given by:

$$U = \sum_j n_j \varepsilon_j = \frac{N}{Z} \sum_j \varepsilon_j e^{\beta \varepsilon_j}. \quad (55)$$

Now, since the partition function is given by:

$$Z = \sum_j e^{\beta \varepsilon_j}, \quad (56)$$

we can write:

$$\frac{dZ}{d\beta} = \sum_j \varepsilon_j e^{\beta \varepsilon_j}. \quad (57)$$

Combining equations (55) and (57) gives:

$$U = \frac{N}{Z} \frac{dZ}{d\beta} = N \frac{d \ln Z}{d\beta}. \quad (58)$$

Entropy and the partition function

The second relation between energy and partition function involves the Helmholtz free energy, F :

$$F = U - TS. \quad (59)$$

First, let's remind ourselves of the significance of the Helmholtz free energy. From the definition of F , we can write:

$$dF = dU - T dS - S dT. \quad (60)$$

Using the first law of thermodynamics, $dU = T dS - p dV$, it follows that:

$$dF = -p dV - S dT. \quad (61)$$

The Helmholtz free energy is constant for a change taking place at constant volume and constant temperature. We see that the entropy and the pressure can be expressed as:

$$S = - \left(\frac{\partial F}{\partial T} \right)_V, \quad p = - \left(\frac{\partial F}{\partial V} \right)_T. \quad (62)$$

Now we can find a relation between the Helmholtz free energy F , and the partition function, Z . Starting from the relationship (58) between internal energy U and the partition function:

$$U = N \frac{d \ln Z}{d\beta}$$

we write:

$$N d(\ln Z) = U d\beta = U d\beta + \beta dU - \beta dU. \quad (63)$$

The first two terms on the right give the derivative of βU :

$$N d(\ln Z) = d(\beta U) - \beta dU. \quad (64)$$

Hence:

$$\beta dU = d(\beta U) - N d(\ln Z). \quad (65)$$

Now, substituting from:

$$\beta dU = -\frac{dU}{kT} = -\frac{dS}{k} \quad (66)$$

into equation (65) we find:

$$dS = -k d(\beta U) + Nk d(\ln Z) = d\left(\frac{U}{T} + Nk \ln Z\right). \quad (67)$$

Now, if we assume that $S \rightarrow 0$ as $T \rightarrow 0$ (as required by the third law of thermodynamics), then we can integrate equation (67) to give:

$$S = \frac{U}{T} + Nk \ln Z, \quad (68)$$

or:

$$F = U - TS = -NkT \ln Z. \quad (69)$$

This equation relates the partition function Z to the Helmholtz free energy F . The entropy and the pressure may then be found from (62).

Summary

You should be able to:

- Explain that thermodynamics describes systems using macroscopic variables to specify macrostates, but in statistical mechanics, the state of a system is specified as a microstate, by giving the energy of each of the particles.
- Tabulate the distributions and microstates of a system with given energy levels, given the number of particles and total energy.
- Apply the formula for the number of microstates within a given distribution.
- State the basic assumptions of statistical mechanics, including the principle of equal a priori probabilities.
- Explain that for systems with many particles, there is a single distribution that contains many more microstates than any other, and that this is the distribution in which the system is most likely to be found.
- Derive the Boltzmann distribution.
- Write the formula for the partition function.
- Explain the relationships between number of microstates and entropy, and the distribution parameter β and thermodynamic temperature.
- Give the relationships between energy and partition function.

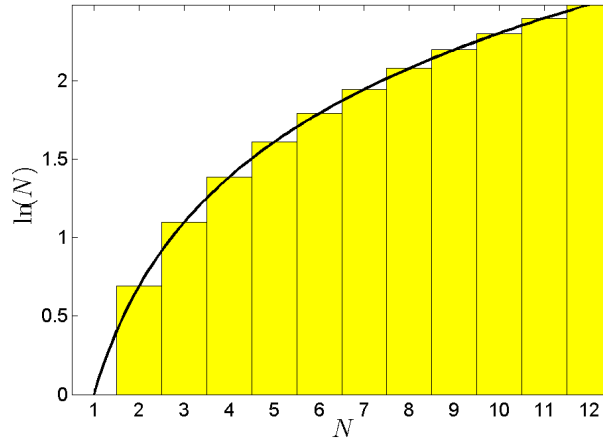
Appendix A: Notation

ϵ_j	Energy of the j^{th} energy level in a system.
n_j	Number of particles occupying the j^{th} energy level in a system.
$N = \sum_j n_j$	Total number of particles in a system.
$U = \sum_j n_j \epsilon_j$	Total energy of a system.
t_i	Number of accessible microstates within a distribution.
$\Omega = \sum_i t_i$	Total number of microstates accessible to a system.
$Z = \sum_j e^{\beta \epsilon_j}$	Partition function.
$\beta = -1/kT$	Distribution function.
$S = k \ln \Omega$	Entropy.
T	Thermodynamic temperature.
$k = 1.3806 \times 10^{-23} \text{ J/K}$	Boltzmann's constant.

We begin by writing:

$$\ln N! = \ln 1 + \ln 2 + \ln 3 + \cdots + \ln N. \quad (70)$$

For large N , the right hand side is approximately equal to the area under the curve $\ln x$, from $x = 1$ to $x = N$.



Hence, we can write:

$$\ln N! \approx \int_1^N \ln x \, dx. \quad (71)$$

Performing the integral:

$$\int_1^N \ln x \, dx = [x \ln x - x]_1^N = N \ln N - N + 1. \quad (72)$$

Since we are assuming that N is large,

$$N \ln N - N + 1 \approx N \ln N - N, \quad (73)$$

and hence, for large N :

$$\ln N! \approx N \ln N - N. \quad (74)$$

This is Stirling's approximation.